the rate constant is probably a reflection of the methyl migration and not an accurate measure of the self-exchange rate constant between two molybdenum centers. The self-exchange rate must be slower than the rate of methyl migration to a CO. The reported value for self-exchange of methyl between two tungsten centers is also quite slow.[6a]

The equilibrium constant for the cross reaction,

$$CpFe(CO)_2^- + MeMoCp(CO)_3 \rightarrow MeFeCp(CO)_2 + CpMo(CO)_3^- \quad (9)$$

is also required. For this reaction there is no trace of the reactants by ^1H NMR or IR spectroscopy after the reaction, indicating an equilibrium constant that is large, at least $>10^4$. Using the pK_a values[4] as a means to approximate the equilibrium constant gives a value of $K_{eq} = 10^6$. Using this value for K_{eq} and the self-exchange values of k_1 (for Fe, reaction 6) = 50 s^{-1} M^{-1} and k_2 (for Mo, reaction 7) $<5.3 \times 10^{-4}$ s^{-1} M^{-1} gives

$$k_{12} = [(50\ s^{-1}\ M^{-1})(5.3 \times 10^{-4}\ s^{-1}\ M^{-1})(10^6)]^{1/2} = 200\ s^{-1}\ M^{-1}$$

This value is in moderate agreement with the observed value of 1100 s^{-1} M^{-1}. Thus the methyl transfer may obey relative Marcus-type relationships, but uncertainty in the value for the $CpMo(CO)_3^-/CpMo(CO)_3Me$ self-exchange rate constant and in the equilibrium constant for reaction 9 prohibits a more detailed analysis. Similar analysis for CH_3^+ transfer between two organic nucleophiles[26] indicates reasonable utility of eq 5 for methyl-transfer reactions.

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Conclusion

The results reported in this paper show that transfer of alkyl groups between metal carbonyl anions is closely related to organic nucleophilic displacement reactions in reactivity and mechanism. This represents the first comparison of transfer of different alkyl groups between transition metal centers.

Acknowledgment. We are grateful to the Department of Energy, Office of Basic Energy Sciences (DE-FG02-87ER13775.A004), for support of this research. The Varian VXR-400 NMR spectrometer was purchased with funds from the Department of Education (2-2-01011).

Supplementary Material Available: Plots of the absorbance change at 1790 cm^{-1} for reaction of $MeMn(CO)_5$ with $CpFe(CO)_2^-$, $[MeMn(CO)_5]$ versus k_{obsd}, and line width of the Cp resonance of $CpFe(CO)_2^-$ versus $[MeFeCp(CO)_2]$ for the self-exchange reaction (3 pages). Ordering information is given on any current masthead page.

Multichromophoric Cyclodextrins. 1. Synthesis of *O*-Naphthoyl-β-cyclodextrins and Investigation of Excimer Formation and Energy Hopping

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Abstract: The synthesis and photophysical properties of β-cyclodextrins bearing seven 2-naphthoyloxy chromophores in specific positions, either on the primary face or the secondary face, or 14 2-naphthoyloxy chromophores, seven on each face, are reported. These multichromophoric cyclodextrins are good models for the study of excitation energy migration among chromophores in well-defined positions. The investigation was performed in dichloromethane and in a mixture of ethanol and methanol that can form a glass at low temperature. The absorption spectra show that the interactions between chromophores in the ground state are weak, whereas the fluorescence spectra reveal the existence of excimers at room temperature but not at low temperature in a rigid glass. Further evidence of excimer formation is provided by the fluorescence decays. Since excimers act as energy traps, the energy hopping process was studied in a rigid glass at low temperature by steady-state and time-resolved fluorescence depolarization techniques. The steady-state anisotropy is found to be one seventh of the theoretical limiting anisotropy 0.4, which means that excitation energy hops between chromophores with essentially randomly oriented transition moments at a rate much higher than the chromophore intrinsic decay rate. Energy hopping is indeed very fast as shown by the fluorescence anisotropy decay which is at least as fast as the apparatus time resolution (a few tens of picoseconds).

Introduction

In recent years, there has been a great deal of activity devoted to supramolecular photophysics and photochemistry.[1-4] Among the systems investigated, cyclodextrins (CD's) (cyclic oligosaccharides composed of six (α-CD), seven (β-CD), or eight (γ-CD) D-(+)-glucopyranose units) have been the object of special attention because of their ability to form supramolecular species by enclosing various compounds undergoing specific photoprocesses.[3,5,6]

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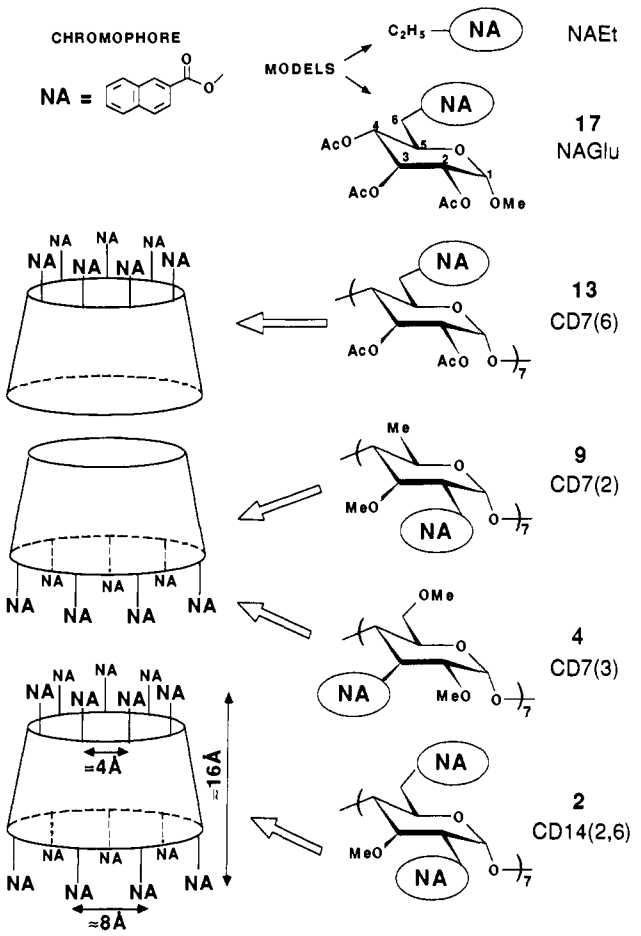


Figure 1. Chemical structure of the model compounds and the *O*-naphthoyl-β-CD's. The latter are denoted by CD$x(y)$ where x is the number of chromophores and y is the position of the chromophores with respect to the glucopyranose unit (numbered in the usual way). NA is the symbol for the naphthoyloxy chromophore.

In the present paper, we report the synthesis and photophysical properties of β-CD's bearing seven 2-naphthoyloxy chromophores in specific positions, either on the primary face or the secondary face, or 14 2-naphthoyloxy chromophores (NA), seven on each face (see Figure 1). Because of the close distance between the chromophores, these modified cyclodextrins are expected to undergo very fast energy hopping following electronic excitation. These systems thus offer interesting models for a better understanding of excitation energy transport involving a limited number of excitable species with defined positions. This process is relevant to the antenna effect involved in photosynthetic systems and in photochemical molecular devices.[3,7,8]

Most of the previous investigations on excitation energy transport have been carried out with polymers having chromophores substituted at intervals along the chains (for reviews, see refs 9–11); in these systems, energy transfer occurs between nearest-neighbor chromophores and also between any two chromophores that are close together in space but far removed from each other along the chain because of chain coiling. In the labeled β-CD's described in this work, the position of the chromophores is much better spatially defined, and the limited number of chromophores in a circular arrangement is a distinct advantage for the interpretation of the photophysical results. The average interchromophoric distance being about 4 Å on the primary face and 8 Å on the secondary face, energy migration is expected to be efficient by either dipole–dipole interaction or exchange interaction. Owing to the circular arrangement of the chromophores, the interactions between nearest neighbors should be most predominant.

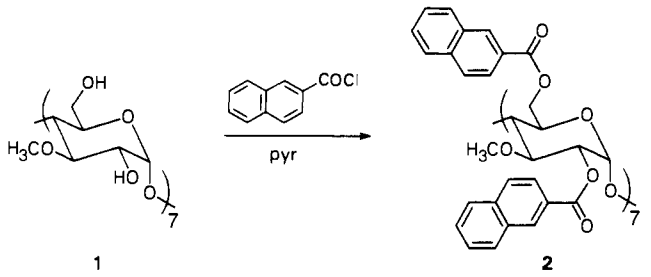
As in the case of polymers, the close distance between chromophores in the labeled β-CD's favors excimer formation, although appropriate mutual orientation and separation are necessary. Excimers act as energy traps, thus reducing energy-hopping efficiency.

The design of multichromophoric β-CD's deserves special attention. Although appearing relatively free, the choice of the final substrates to be synthesized underwent two types of constraints. The photophysical one forbids introduction of any chemical group which could significantly interfere in the fluorescence properties of the naphthoate chromophores (by quenching for instance). The synthetic constraints are related to the difficulties encountered in the cyclodextrin chemistry. Recently, a number of selectively O-substituted cyclodextrins were reviewed.[12] The main entries to the β-cyclodextrin functionalization result from the selective reaction either of the position 6 (essentially by introduction of several leaving groups) or of the positions 2 and 6 (O-alkylations and esterifications). As the naphthoyl ester group can be introduced either by esterification of an alcohol with a β-naphthoic acid derivative or by nucleophilic substitution of a leaving group by a β-naphthoate, a synthetic way was easily devised for the 3- and 6-heptanaphthoyl and for the 2,6-tetradecanaphthoyl-β-cyclodextrin derivatives (**4**, **11**, and **2**, respectively). The synthesis of the 2-heptanaphthoyl-β-cyclodextrin **9** is much more demanding as it requires the total differentiation of all the alcohol positions.

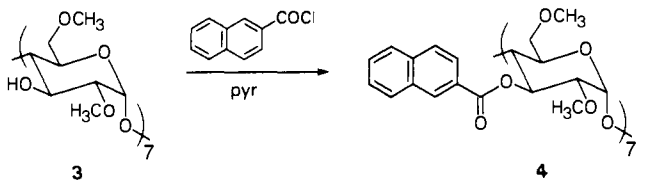
In this paper, the synthesis and the photophysical properties of these *O*-naphthoyl-β-cyclodextrins are described. Steady-state absorption and fluorescence measurements as well as time-resolved fluorescence experiments, in time domain and frequency domain, provide information on chromophore interactions in the ground and excited states. Measurements of steady-state and time-resolved fluorescence anisotropy were used to characterize the energy-hopping dynamics.

Synthesis of *O*-Naphthoyl-β-cyclodextrins. The *O*-naphthoyl-β-cyclodextrins (**2**, **4**, **9**, and **13**) were synthesized by esterifications of modified β-CD's (**1**, **3**, **8**, and **12**). They were characterized by a battery of methods: FABMS, thin-layer chromatography (TLC), elemental analysis, and chiefly by their ^{1}H and ^{13}C NMR spectrum which are remarkably simple because of the 7-fold symmetry of these compounds (see Experimental Section). The main difficulties in most of these syntheses arose

Scheme I



Scheme II



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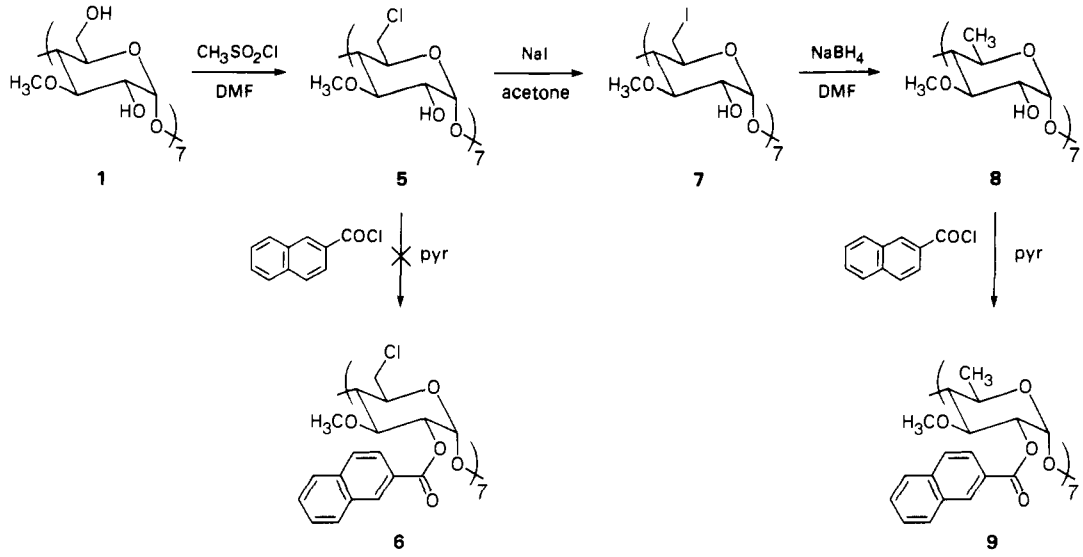
Scheme III



in the purification of the final products (column chromatography, TLC, and crystallization).

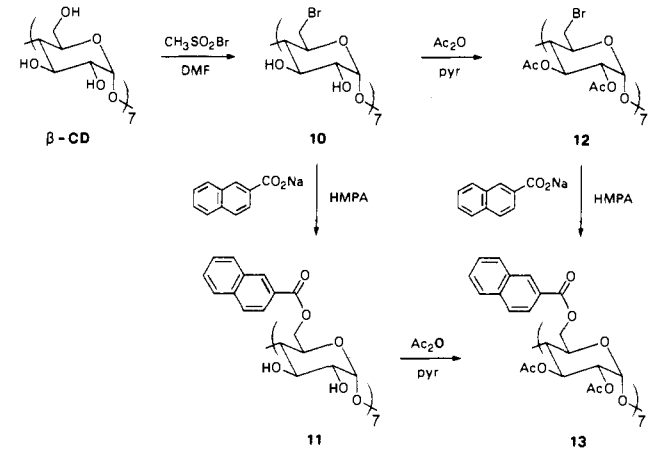
The per(2,6-*O*-naphthoyl)-β-CD derivative **2** was prepared in 50% yield by treatment of per(3-*O*-methyl)-β-CD **1** with 2-naphthoyl chloride in dry pyridin (80 °C, 5 days) (Scheme I). **1** was obtained in the course of other work in three steps from β-CD by selective per(2,6)-O-benzylation, followed by per-3-O-methylation, and then hydrogenolysis at the 14 benzyl groups.[13]

Treatment of per(2,6-*O*-methyl)-β-CD **3** (commercially available) under the same conditions as for **1** afforded the per-(3-*O*-naphthoyl)-β-CD **4** in 25% yield after very tedious chromatographic purifications (Scheme II).

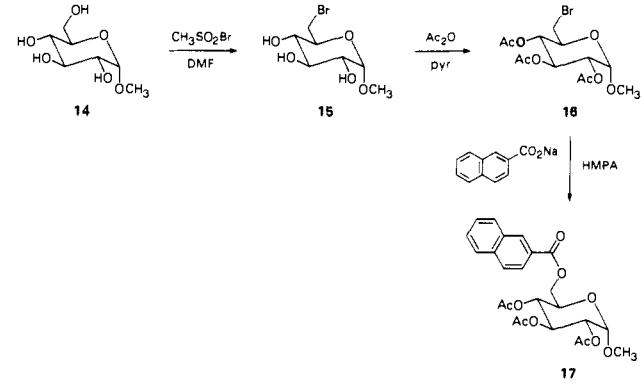
To introduce the naphthoyl group in position 2, per(3-*O*-methyl)-β-CD **1** was used as starting material and treated with methanesulfonyl chloride (as described for the preparations of some methyl 6-chloro-6-deoxyglycosides to afford the conveniently differentiated precursor, per(6-chloro-6-deoxy)per(3-*O*-methyl)-β-CD **5**.[14] Unfortunately, reaction of **5** with 2-naphthoyl chloride under the usual conditions did not yield the expected naphthoate **6** but only untractable mixtures. Therefore, it was decided to reduce the chloromethyl into methyl groups. This reduction being very difficult, chloride **5** was converted into iodide **7** (NaI; butanone; reflux 3 days) which was treated with sodium borohydride in DMF according to the Takeo procedure,[15] to give per(6-deoxy)per(3-methyl)-β-CD **8**. This compound was then esterified, as above, with naphthoyl chloride to afford the per-(3-*O*-naphthoyl)-β-CD derivative **9** in 45% yield (Scheme III).

The shortest access to per(6-*O*-naphthoyl)-β-CD derivatives resides in the selective activations of the 6-OH positions followed by nucleophilic displacement with the naphthoate anion. The per(6-*O*-naphthoyl)-β-CD **13** was synthesized in three steps from β-CD. The selective bromination of the primary OH groups of β-CD with methanesulfonyl bromide in DMF afforded per(6-bromo-6-deoxy)-β-CD **10**.[15] Treatment of this bromide **10** with sodium naphthoate in HMPA gave the expected compound **11**, which however could not be easily purified and characterized (these difficulties being undoubtedly due to the 14 free OH groups). Therefore, **11** was acetylated (acetic anhydride in pyridin; room temperature 24 h) to yield the peracetylated derivative **13**. At this stage, it appeared much more convenient to acetylate directly the heptabromide **10** into per(6-bromo-6-deoxy)per(2,3-*O*-acetyl)-β-CD **12** which, upon treatment with sodium naphthoate, yielded the desired compound **13** in 45% yield (Scheme IV).

Scheme IV



Scheme V



The model compound **17** was obtained from methyl α-D-glucopyranoside **14** which was converted into bromide **15** by reaction with methanesulfonyl bromide. Treatment of **15** with acetic anhydride in dry pyridin[14] gave **16**, which after reaction with sodium naphthoate in HMPA afforded **17** in almost quantitative yield (Scheme V).

Results of the Photophysical Studies. For the sake of clarity, the *O*-naphthoyl-β-CD's are denoted by CD*x*(*y*) where *x* is the number of chromophores and *y* is the position of the chromophores with respect to the glucopyranose unit (numbered in the usual way).

Absorption and Excitation Polarization Spectra. Ultraviolet absorption spectra (250–350 nm) were recorded in dichloromethane and in a mixture (9:1 v/v) of ethanol and methanol

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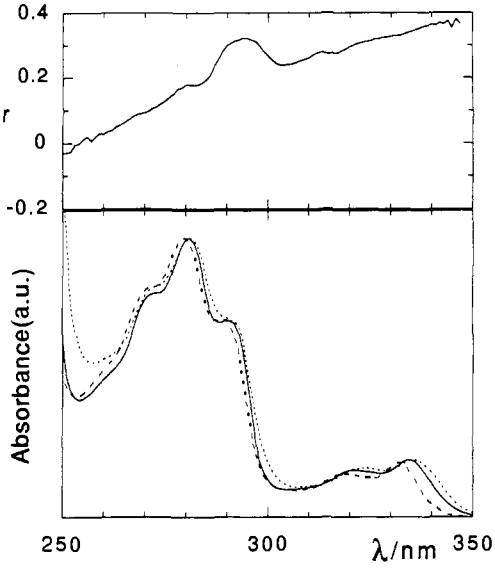

Figure 2. Bottom: absorption spectra of NAGlu (—), CD7(3) (— —), and CD7(6) (– –) in ethanol–methanol 9:1 v/v at 290 K. Top: excitation polarization spectrum of NAGlu in ethanol–methanol 9:1 v/v at 100 K (rigid glass).

(subsequently noted EM) at room temperature. They are very similar for all compounds (Figure 2) and characteristic of 2-substituted naphthalenes.[16] The first electronic band ($^1L_b \leftarrow {}^1A$) with maxima at 332–336 and 320–323 nm, the exact values depending on the compound, has a molar absorptivity at the absolute maximum (332–336 nm) of ca. 1500 $M^{-1}\cdot cm^{-1}$ per chromophore. The second electronic band ($^1L_a \leftarrow {}^1A$), with maxima at 290, 280, and 268 nm, has a molar absorptivity at the absolute maximum (280 nm) of ca. 7200 $M^{-1}\cdot cm^{-1}$ per chromophore. Excitation spectra in the EM glass at 100 K are identical to the room temperature absorption spectra, minor wavelength shifts (<2 nm) being observed in the first band, along with some narrowing that makes further vibronics at 327 and 305 nm barely perceptible for the model compounds NAEt and NAGlu; these vibronic bands are also observed in NAEt in cyclohexane at room temperature. The existence of vibronic structure in all cases, including the multichromophoric β-CD's, shows that planarity between the ring and the carboxy group is retained.[17] The excitation polarization spectrum of NAGlu in the alcoholic glass at 100 K (Figure 2) shows that the first band ($^1L_b \leftarrow {}^1A$) is mainly short axis polarized, although vibronic coupling with the strong ($^1B_b \leftarrow {}^1A$) band, which occurs at ca. 240 nm, progressively decreases the emission anisotropy. This quantity rises again at the 0–0 transition of the second band ($^1L_a \leftarrow {}^1A$), which is also mainly short axis polarized: from the anisotropy ratio of the 0–0 transitions of $^1L_a \leftarrow {}^1A$ and $^1L_b \leftarrow {}^1A$ bands, the angle between the respective transition moments is estimated to be 16°, which is equal to the theoretical value computed for 2-naphthol.[18] Below 290 nm, the monotonous decrease of anisotropy toward negative values is again a result of vibronic coupling with the strong $^1B_b \leftarrow {}^1A$ band, long-axis polarized.[19] The overall polarization pattern is identical to that observed for NAEt and also for other 2-substituted naphthalenes with strongly conjugating groups.[19] In regards to the multichromophoric β-CD's, it will be shown below that the excitation polarization spectrum is strongly affected by interchromophoric energy transfer.

From the similarity of the absorption spectra of the multichromophoric cyclodextrins with those of the model compounds (NAEt and NAGlu), it can be concluded that the interactions between chromophores in the ground state are weak, i.e., with a

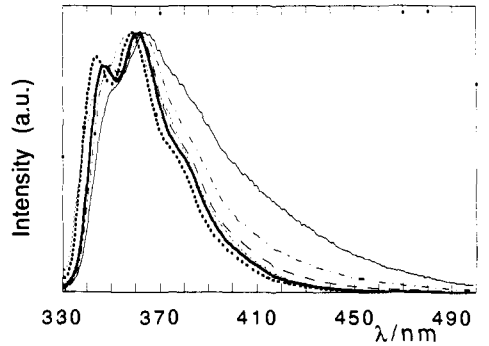

Figure 3. Emission spectra of NAGlu (—), NAEt (• • •), CD7(3) (– – –), CD7(2) (— —), CD7(6) (— • —) and CD14(2,6) (—) in dichloromethane.

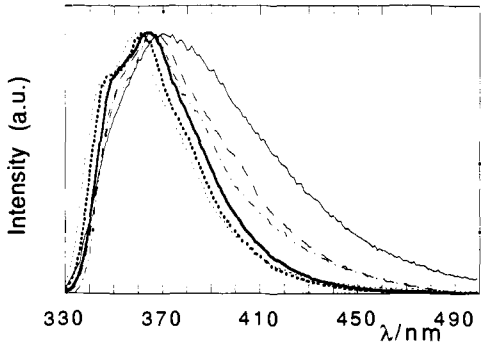

Figure 4. Emission spectra of NAGlu (—), NAEt (• • •), CD7(3) (– – –), CD7(2) (— —), CD7(6) (— • —) and CD14(2,6) (—) in ethanol–methanol 9:1 v/v at 290 K.

magnitude smaller than the optical line width.

Fluorescence Spectra and Quantum Yields. Contrary to what happens with absorption, the emission of the compounds shows remarkable variety and is solvent dependent. In dichloromethane at room temperature (Figure 3), one can distinguish several situations. On the high energy side, though not all spectra coincide, vibrational structure is apparent for all but CD7(3) and CD14-(2,6), which show only a slight shoulder before the emission maximum. On the low energy side, CD7(2), CD7(6), and CD14(2,6) present extended tails, especially the latter, as a result of excimer formation. Indeed, concentrated ($>10^{-2}$ M) solutions of NAEt in cyclohexane exhibit similar tails, due to intermolecular excimer formation. This excimer emission has a maximum near 400 nm, i.e., not very far from the monomer emission, which explains the broadening of the emission spectra of the β-CD's instead of the appearance of a new band (as in the case of pyrene). In other CD's systems bearing two 2-naphthoate chromophores, excimer emission was also reported.[20,21]

In EM at room temperature (Figure 4), where in contrast to dichloromethane the solubility is low, besides a small red-shift and loss of vibrational structure as a result of increased solute–solvent interactions (including hydrogen bonding), it is observed that for CD7(2) and again CD7(6) and CD14(2,6) a large fraction of the emission lies beyond 420 nm owing to excimer formation. It should be noted that contrary to all other compounds, CD7(3) shows almost no change in its emission spectrum when going from dichloromethane to the alcoholic mixture, apart from a slight increase of the red-edge tail.

In both solvents, no significant differences were detected between the absorption spectra and the excitation spectra recorded for various observation wavelengths (including the red part of the emission spectrum where excimer emission is predominant). This further confirms that the interactions between chromophores are

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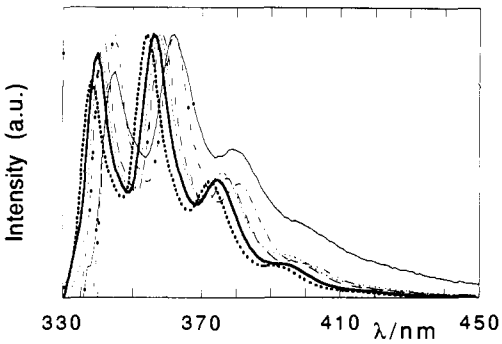

Figure 5. Emission spectra of NAGlu (—), NAEt (•••), CD7(3) (• • •), CD7(2) (— —), CD7(6) (— · —) and CD14(2,6) (—) in ethanol–methanol 9:1 v/v at 100 K (rigid glass).

weak in the ground state; in particular, there is no ground-state naphthoyloxy dimer.

Fluorescence quantum yields in EM at 290 K were found to be 0.42 for NAEt, 0.41 for NAGlu, 0.40 for CD7(2), 0.42 for CD7(3), 0.28 for CD7(6), and 0.39 for CD14(2,6). Within experimental error (±0.02), a common value is thus obtained for all compounds (0.40) with the sole exception of CD7(6), which has a distinctly lower quantum yield. Note that in the cases where excimer exists, the quantum yield contains an excimer contribution.

Emission in the EM glass at 100 K are well structured and similar to that of NAEt in cyclohexane at room temperature; they are in general blue-shifted with respect to the room temperature ones (Figure 5), the only exception being CD7(3) for which no shift is observed. The disappearance of the red-edge tail corresponding to excimer emission is noticeable for CD7(2) and CD7(6) but not for CD14(2,6). As for the room temperature spectra, it can be concluded that this compound has a spectroscopic behavior that is not the mere superimposition of those of CD7(2) and CD7(6). However, the persistence of excimer emission in the glass for the 14-chromophore compound could also be of intermolecular origin, owing to its very low solubility in the solvent (5×10^{-7} M at room temperature) and consequent possible formation of aggregates on cooling. Intermolecular excimer emission was indeed observed for CD7(3) in glycerol at room temperature, where its solubility is very poor; the strong excimer band with a maximum at 422 nm is to be compared with the excimer emission for crystalline 1-naphthoic acid, with a maximum at 429 nm.[17] The excimer band of CD7(3) is even selectively excitable at wavelengths longer than 340 nm, i.e., beyond monomer absorption. This is an evidence for the presence of ground-state dimers which yield a strongly red-shifted excimer emission. These dimers are presumably formed in aggregates or microcrystals of CD7(3) and are of intermolecular origin. Although the geometry of ground-state dimers and excimers is not the same,[22] interconversion should readily occur; for crystalline pyrene, molecular readjustment was reported to take 140 fs.[23] Further evidence for the intermolecular origin of the excimer emission is provided by the emission of CD7(3) in aqueous micellar solutions of sodium dodecyl sulfate (SDS), 0.1 M in sodium chloride. For high CD7(3)/SDS ratio, the excimer tail is present, while it is absent for low ones, when no more than one molecule is associated with a (presumably perturbed) SDS micelle.

Fluorescence Decays. Fluorescence decays of NAEt and NAGlu are single exponential in all cases (Table I). On the other hand, multichromophoric β-CD's have complex decays which are even emission wavelength dependent in some cases (Tables II and III). Analysis of the data was performed by a nonlinear least-squares method and by the maximum entropy method. These methods yield very close values of the decay time constants and fractional intensities. It should be recalled that in the maximum entropy method, there is no a priori assumption on the form of the decay,[24,25] and, in particular, distributions of decay times can be recovered. Therefore, the results obtained with the β-CD's demonstrate that all the decays consist indeed of a sum of two or three exponentials and not a distribution (see Figure 6 for illustration).

Table I. Fluorescence Lifetimes (ns) of the Model Compounds (NAEt and NAGlu) in Several Solvents Measured by the Phase-Modulation Technique at 290 K (Degassed Solutions)

	dichloromethane	ethanol–methanol 9:1 v/v	cyclohexane
NAEt	6.7	11.2	14.9
NAGlu	5.8	10.8	

Tables II and III show that a sum of at least two exponentials is necessary for a satisfactory fit to the decay curves of the β-CD's, even in the absence of excimer formation (e.g., CD7(3) in dicholoromethane). The dominant decay time is close to that of NAEt and NAGlu. The smaller component may arise from the existence of a different conformer. In the presence of excimer formation (e.g., CD7(2) in dichloromethane and EM) the decay is emission wavelength dependent, and a third component with a longer decay time appears. This component is attributed to the excimer, as it becomes predominant in the red part of the emission. It is important to note that no risetime was detected in the shortest time scale available with our instrumentation (a few tens of picoseconds), even in the red-edge of the emission. This point will be discussed below.

Decays at low temperature (100 K) were also obtained in EM for some compounds. The fluorescence decay of NAGlu is again a single exponential (13.4 ns); the cyclodextrins CD7(3) and CD7(6), which are excimer-free (see Figure 5), also exhibit single exponential decays (15.3 and 12.1 ns, respectively), in contrast to room temperature results. These values are higher than at room temperature, owing to the normal decrease of the nonradiative decay processes.

Steady-State and Time-Resolved Fluorescence Anisotropy. In fluid solution (ethanol–methanol at 290 K) the measured anisotropy is virtually zero for all compounds. This complete depolarization is due to the rotational motion of the chromophores within the excited state lifetime. This motion is frozen in the EM glass at 100 K, as evidenced by the NAEt and NAGlu high anisotropies. For these compounds the emission anisotropy is indeed about 0.36 (maximum observed: 0.38) at high excitation wavelengths, i.e., close to the theoretical limit of 0.40 pertaining to colinear absorption and emission transition moments. In contrast, the emission anisotropy of the four substituted β-CD's is considerably lower, as a result of energy transfer; the common value is found to be close to 0.06 upon excitation at the S_1 0–0 transition (Figure 7). A lack of depolarization by energy transfer is observed upon excitation at the absorption red-edge for three of the cyclodextrins. This phenomenon, known as the red-edge effect, was first observed by Weber and is attributed to solvation heterogeneity.[26-28]

The fluorescence anisotropy decay for CD7(3) in the EM glass at 100 K (Figure 8) is very fast with respect to the fluorescence lifetime (15.3 ns): the decay time of the initial decrease is <20 ps, i.e., shorter than the apparatus time resolution. Another smaller component is detected at 0.48 ns. The anisotropy decay does not tend to be near zero at long times but to a limiting value of 0.069.

Discussion

Excimer Formation. Two types of excimers are a priori possible in labeled β-CD's: (a) preformed excimers, requiring minimum adjustments of distance and orientation, and (b) rotational ex-

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Table II. Fluorescent Decay Components (ns) of the β-CD's in Dichloromethane at 290 K at Different Observation Wavelengths[a]

	366 nm		402 nm		447 nm	
	MEM	LS	MEM	LS	MEM	LS
CD7(3)	3.3 (5%)	2.0 ± 0.5 (3%)			2.1 (7%)	1.9 ± 0.1 (16%)
	7.2 (95%)	7.1 ± 0.2 (97%)			7.2 (93%)	9.0 ± 0.1 (84%)
CD7(2)	4.0 (36%)	4.3 ± 0.1 (40%)			—	—
	7.7 (64%)	8.1 ± 0.1 (60%)			7.1 (63%)	7.4 ± 0.1 (62%)
	—	—			18.9 (37%)	18.6 ± 0.9 (38%)
CD7(6)	1.9 (4%)	1.5 ± 0.1 (5%)	1.8 (1%)	2.3 ± 0.6 (3%)		—
	6.1 (70%)	6.3 ± 0.2 (64%)	6.4 (51%)	7.0 ± 0.4 (52%)	—	—
	14.1 (26%)	14.0 ± 0.6 (31%)	15.0 (48%)	15.6 ± 0.5 (45%)	14.1 (100%)	14.0 ± 0.1 (100%)
CD14(2,6)	1.7 (3%)	1.6 ± 0.2 (6%)			—	—
	5.5 (49%)	6.2 ± 0.4 (62%)			—	—
	11.0 (47%)	13.5 ± 1 (32%)			13.4 (100%)	13.7 ± 0.1 (100%)

[a] Measurements by phase modulation technique and analysis by the maximum entropy (MEM) and nonlinear least squares (LS) methods. The fractional intensities are indicated in parentheses. Satisfactory values of the reduced χ-squared are found in all cases.

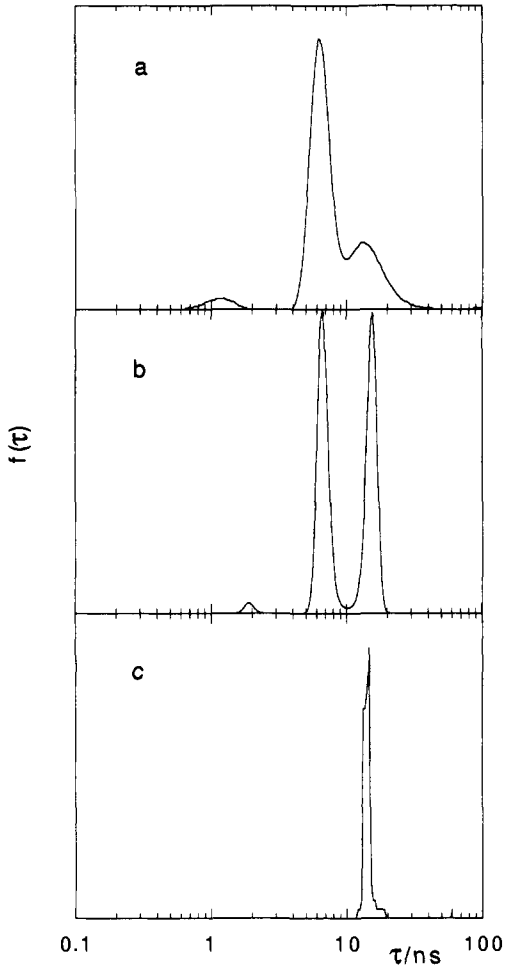

Figure 6. Results of data analysis by the maximum entropy method in the case of CD7(6) in dichloromethane at 290 K. The emission wavelength is 366 (a), 402 (b), and 447 nm (compare Table II).

cimers requiring significant internal rotation around bonds before the excimer geometry can be reached. While the distinction between these two types is not clear-cut, type **a** must be said to be characterized by extremely short rise-times (i.e., a few picoseconds at most) in the excimer time-evolution and almost no viscosity dependence and type **b** by longer rise-times (nano- or subnanosecond time scale) and significant viscosity dependence of the displacement of solvent molecules by the chromophores in their path to the excimer configuration.

From the room-temperature emission spectra it can be concluded that excimer emission exists, in an increasing order, for CD7(2), CD7(6), and CD14(2,6) in both dichloromethane and EM and probably for CD7(3) in EM. The strongest excimer emission observed for CD14(2,6) is probably due to especially suited conformations favored by the existence of 14 chromophores.

Table III. Fluorescent Decay Components (ns) of the β-CD's in Ethanol–Methanol (9:1 v/v) at 290 K at Two Observation Wavelengths[a]

	366 nm	402 nm
CD7(3)	4.9 (3%)	1.6 (3%)
	12.5 (97%)	14.7 (97%)
CD7(2)	1.4 (2%)	3.8 (5%)
	8.5 (64%)	9.4 (41%)
	19.6 (34%)	24.1 (54%)
CD7(6)	1.6 (4%)	2.0 (2%)
	9.4 (64%)	8.5 (26%)
	21.0 (34%)	18.9 (72%)
CD14(2,6)	1.1 (9%)	2.4 (5%)
	11.6 (51%)	9.8 (15%)
	24.1 (40%)	21.7 (80%)

[a] Measurements by phase modulation technique and analysis by the maximum entropy. The fractional intensities are indicated in parentheses. Satisfactory values of the reduced χ-squared are found in all cases.

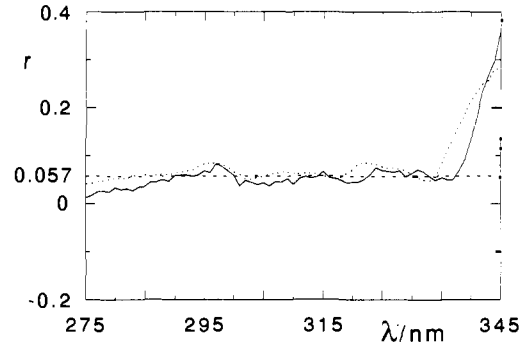

Figure 7. Excitation polarization spectrum of CD7(2) (—) and CD7(3) (--) in ethanol–methanol 9:1 v/v at 100 K (rigid glass). The theoretical value 0.4/7 = 0.057 is indicated by a broken line parallel to the wavelength axis.

The possible intermolecular supplementary contribution can be ruled out as no ground-state dimers or a concentration effect were detected. Also, the wavelength corresponding to the maximum of the excimer emission is again 400 nm, in contrast to the maximum observed at 422 nm for CD7(3) in glycerol.

Further evidence of excimer formation is provided by the fluorescence decays which exhibit a long component predominant in the red part of the emission spectra. As no rise-time is detected, it can be concluded that excimers are preformed, as previously reported for other multichromophoric systems.[29,30] However, no evidence was found for ground-state dimers as observed in some bichromophoric molecules by Reynders et al.[31] and here for

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CD7(3) in glycerol. Indeed, the emission spectrum of CD7(2) and CD7(6) is insensitive to the excitation wavelength, and the absorption shows no extended tail beyond 340 nm as in glycerol. The observation that at 100 K no excimer emission appears (except for CD14(2,6), vide supra) means that a small displacement of the chromophores, hindered at 100 K, is thus required for excimer formation. The fact that the monomer decay contains the model compound lifetime as the main component, even in the presence of excimer, leads to the conclusion that two classes of chromophores exist: those in the form of preformed excimers and those which cannot form excimers.

Also, as fast energy migration should always end in excimer emission owing to energy trapping by the (irreversible) preformed excimers, and monomer emission is observed, we conclude that preformed excimers do not occur in every molecule, i.e., their average number per cyclodextrin is smaller than unity. This is confirmed by estimating the fractional intensity due to the excimer, the excimer spectrum being obtained by subtracting the NAGlu emission to the CD's emission. The sole exception is CD14(2,6) in EM where excimer emission accounts for ca. 50% of the photons emitted, thus possessing at least one excimer in one of its faces, and none on the other (interfacial migration is ruled out by the polarization results).

Energy Hopping. The drastic depolarization observed for the β-CD's in the glass is due to electronic energy transfer, i.e., energy hopping from one chromophore to another. In the case of randomly oriented chromophores undergoing efficient energy transfer, the acceptor steady-state anisotropy is expected to be close to zero.[32] The fact that the observed anisotropy, 0.06 ± 0.01 is approximately equal to one-seventh of the theoretical limiting anisotropy, 0.4 (i.e., 0.4/7 = 0.057),[33] fits with a model of fast energy hopping between seven chromophores with essentially randomly oriented transition moments. Indeed, invoking the additive property of anisotropy, one has $r = \sum f_i r_i$, where f_i is the fraction of light emitted by the ith species, with anisotropy r_i; in the present case, owing to the rapidity of transfer (see below), an excited state equilibrium is rapidly attained, each chromophore contributing with 1/7 to the global intensity. As the six indirectly excited naphthoates have essentially unpolarized emission ($r_i \approx 0$), the overall anisotropy has the value given above, 0.4/7.

The fact that for CD14(2,6) the measured anisotropy is close to 0.4/7 but not to 0.4/14 shows that, within the naphthoate lifetime, energy transfer is fast on each face but so slow as to be negligible between faces, in agreement with the relatively high separation distance (16 Å). The existence of excimer formation in this compound may also lead to a decrease of the face-to-face transfer contribution to anisotropy, as when a preformed excimer exists in one of the faces, excitation will be trapped by it, and no contribution to monomer anisotropy will result from the jump between faces. Evidence for the existence of preformed excimers in CD14(2,6) is the anisotropy increase for wavelengths above 390 nm not observed for the other compounds. As the overall anisotropy is again the average over directly and indirectly excited excimers, the intrinsic anisotropy of these is higher than the observed value.

From the steady-state anisotropy data, it is concluded that excitation energy hops between chromophores at a rate much higher than the chromophore intrinsic decay rate; in other words, the excitation energy has a very short residence lifetime on a chromophore. This important point will be now discussed in terms of interchromophoric distances in conjunction with transfer mechanisms.

From molecular models, the average interchromophoric distances are ca. 8 Å for CD7(2) and CD7(3), 4 Å for CD7(6) and 8 Å (2–2), 4 Å (6–6) and 16 Å (2–6) for CD14(2,6). At such short distances energy transfer is indeed expected to be very fast and may occur via either dipole–dipole interaction (Förster's mechanism) or exchange interaction (Dexter's mechanism).[34,35] The latter is efficient only at short distances allowing the orbitals to overlap, whereas the former is still operative at quite long distances depending on the Förster critical radius representing the distance at which energy transfer from the donor moiety and its direct decay to the ground state are equiprobable processes. Because of the inverse sixth power dependence of the transfer rate on distance for Förster's mechanism, and the exponential dependence for Dexter's mechanism, energy hopping is likely to occur between nearest neighbors.

Förster critical radii were estimated to be 14 Å (CD7(3), CD7(6) and 15 Å (CD7(2)) (see Experimental Section); for CD14(2,6), at least two classes of chromophores exist, and direct spectroscopic evaluation of $\bar{R}_0$ is not feasible. However, it may be considered that 2–2 and 6–6 interactions have the radius obtained for the respective moieties, while for 2–6 interactions the average value holds (14–15 Å). According to Förster's theory, the rate constant is given by

$$k_T = \frac{1}{\tau}\cdot\frac{3}{2}\,\kappa^2\left(\frac{\bar{R}_0}{r}\right)^6$$

where τ is the lifetime, κ^2 the orientational factor (with values between 0 and 4), $\bar{R}_0$ the isotropic Förster radius, and r the distance. Crude estimates of the rate constants can be obtained by taking the orientation factor κ^2 equal to the dynamic average, i.e., 2/3,[36] and $\bar{R}_0$ = 14 Å, τ = 14 ns. The reciprocals of the rate constants range from 8 ps (r = 4 Å) to 490 ps (r = 8 Å). As interchromophoric distances may be smaller, and additional transfer mechanisms (e.g., exchange type) operative, the above estimations for the excitation residence times are upper limits of the true ones.

The fluorescence anisotropy decay for CD7(3) in the alcohol glass at 100 K (Figure 8) exhibits indeed a very fast initial decrease with a decay time <20 ps, i.e., shorter than the apparatus time resolution, and the other component at 0.48 ns has a much smaller contribution. As expected from the above interpretation of the steady-state data, the anisotropy levels off at long time. This experiment shows that further studies using techniques with femtosecond time resolution (e.g., up-conversion) are required to fully resolve the fast anisotropy decay in the multichromophoric β-CD's studied. Theoretical calculations are in progress to predict the form of the anisotropy decay.

In conclusion, the present work provides evidence for ultrafast energy hopping between naphthoyloxy chromophores bound to β-CD's. The next step is the study of the antenna effect, i.e., the transfer of excitation energy from antenna chromophores to an acceptor enclosed in the CD's cavity in order to mimick a photosynthetic unit. Experiments are in progress with this aim.

Experimental Section

General Procedures. Microanalyses were performed by the Service Central d'Analyses du CNRS (Vernaison) or by the Service de Microanalyses de l'Université P. et M. Curie (Paris). Melting points were determined on a Kofler Heizbank. Optical rotations were measured with a Perkin-Elmer 241 polarimeter in chloroform stabilized with ethanol, using the sodium D line. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (unless otherwise stated) on a AM 200 SY Bruker spectrometer operating at 200.13 MHz for ^{1}H and 50.3 Hz for ^{13}C; chemical shifts are reported in ppm with protonated solvent as internal reference (^{1}H, $CHCl_3$ in $CDCl_3$ 7.26 ppm, CHD_2COCD_3 in CD_3COCD_3 2.04 ppm, CHD_2SOCD_3 in CD_3SOCD_3 2.04 ppm; ^{13}C, $^{13}CDCl_3$ in $CDCl_3$ 76.9 ppm, $^{13}CD_3COCD_3$ in CD_3COCD_3 29.8 ppm, $^{13}CD_3SOCD_3$ in CD_3SOCD_3 39.6 ppm); coupling constants J are given in Hz; homodecoupling and 2D carbon-proton correlations were used when necessary, to assign ^{1}H and ^{13}C NMR spectra (CD's have been numbered from 1 to 6 and naphthalene from 1′ to 8′, in the usual way). Mass spectra (FAB positive) were performed by the Service de Spectrométrie de Masse du

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(33) The absolute error associated with the steady-state anisotropy is smaller than 0.01 and estimated to be 0.005; however, the emission anisotropy depends slightly on the emission wavelength owing to vibronic effects, and a deviation of ±0.01 accounts for this.
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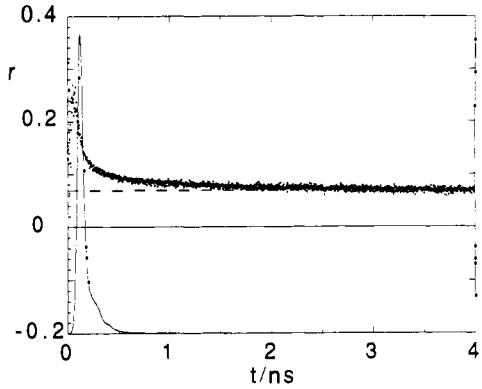

Figure 8. Anisotropy decay curve (dots) of CD7(3) in ethanol–methanol 9:1 v/v at 100 K (rigid glass). The shape of the excitation pulse is shown on a linear scale (channel width, 3.6 ps; excitation wavelength, 300 nm, observation wavelength, 360 nm).

CNRS (Vernaison). Column chromatography was performed on silica gel 60 (0.040–0.063 mm) Merck. Analytical or preparative thin-layer chromatography (TLC) was conducted on Merck silica gel 60 F_{254} precoated plates. Visualization was accomplished with ultraviolet light, iodine, or sulfuric acid (5%). Anhydrous solvents were purchased from SDS and used without further purification. β-Cyclodextrin (β-CD) from Fluka was dehydrated before use. Other commercially available reagents were used as obtained.

$3^A,3^B,3^C,3^D,3^E,3^F,3^G$-Hepta-*O*-methyl-β-cyclodextrin-$2^A,2^B,2^C,2^D,2^E,2^F,2^G,6^A,6^B,6^C,6^D,6^E,6^F,6^G$-tetradecanaphthoate (2). To a solution of per-3-*O*-methyl-β-cyclodextrin **1** (60 mg, 0.05 mmol) in dry pyridine (3.5 mL) was added 2-naphthoyl chloride (400 mg, 2.1 mmol, 3 equiv).[13] The mixture was heated at 70 °C for 7 days. After cooling, water was added. The mixture was extracted with EtOAc. The organic layer was washed with 1 M HCl and with water. Then, it was dried over Na_2SO_4, and the solvent was removed under reduced pressure to afford 375 mg of a brownish oil. The residue was purified by TLC (2-mm plates, CH_2Cl_2–ether 98–2) and then on a short column of silica gel with the same eluent to yield 90 mg (53%) of **2** as a crystalline powder: mp ~190 °C; $[\alpha]^{25}_D$ +88 (*c* 0.6, $CHCl_3$); TLC (CH_2Cl_2–ether 98–2) R_f 0.66 FAB-MS (M + Na^+) calcd 3414, obsd 3414.5; ^1H NMR δ 8.68 (s, 1 H arom), 8.58 (s, 1 H arom), 8.07–7.73 (m, 8 H arom), 7.60–7.36 (m, 4 H arom), 5.72 (d, *J* = 3.0, 1 H, H-1), 5.17–5.08 (m, 2 H, H-2, H-6) 4.90–4.84 (m, 1 H, H-6), 4.58 (m, 1 H, H-4), 4.24–4.16 (m, 2 H, H-3, H-5), 3.48 (s, 3 H, OCH_3); ^{13}C NMR δ 165.97 (COO), 165.95 (COO), 135.41, 132.34, 131.76, 131.22, 129.49, 129.29, 129.11, 128.29, 127.99, 127.59, 127.39, 127.13, 126.71, 126.55, 126.15, 125.25, 125.08 (C arom), 98.01 (C-1), 80.01 (C-3), 78.57 (C-5), 73.79 (C-2), 70.52 (C-4), 63.36 (C-6), 59.98 (OCH_3). Anal. Calcd for $C_{198}H_{168}O_{49}\cdot 2H_2O$: C, 71.13; H, 5.06. Found: C, 71.26; H, 5.12.

$2^A,2^B,2^C,2^D,2^E,2^F,2^G,6^A,6^B,6^C,6^D,6^E,6^F,6^G$-Tetradeca-*O*-methyl-β-cyclodextrin-$3^A,3^B,3^C,3^D,3^E,3^F,3^G$-heptanaphthoate (4). A solution of 133 mg (0.1 mmol) of per(3-6-di-*O*-methyl)-β-cyclodextrin **3** (purchased from Aldrich) and of 150 mg (0.77 mmol, 1.1 equiv) of 2-naphthoylchloride in 5 mL of dry pyridin, was heated 2 days at 70 °C. Then 150 mg more of naphthoylchloride were added, and heating was continued during 2 days. This operation was repeated a third time. After cooling, water was added, and the mixture was extracted with EtOAc. The organic layer was washed with 1 M HCl and then with water. After drying over Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by several silica gel chromatographies (columns and TLC) with use of CH_2Cl_2–acetone 1–1 or CH_2Cl_2–MeOH 9–1 as the eluents, to yield eventually 75 mg (25%) of **4** as a white powder: mp ~200 °C; $[\alpha]^{25}_D$ −372° (*c* 0.485, $CHCl_3$); TLC (CH_2Cl_2–acetone 1–1); R_f 0.1; FAB-MS (M + Na^+) calcd 2433.45, obsd 2433.1, (M + Li^+) calcd 2417.45 obsd 2417.2; ^1H NMR δ 8.58 (s, 1 H, H-1′), 8.02 (d, 1 H, H-3′), 7.76 (d, 1 H, H-5′ or -8′), 7.66 (d, 1 H, H-8′ or -5′), 7.62 (d, 1 H, H-4′), 7.39 (t, 1 H, H-6′ or -7′), 7.26 (t, 1 H, H-7′ or -6′), 5.81 (m, 1 H, H-3), 5.12 (d, *J* = 3.1, 1 H, H-1), 4.25 (m, 1 H, H-5), 4.08 (m, 2 H, H-4, H-6), 3.75 (m, 1 H, H-6), 3.50 (s, 3 H, OCH_3), 3.40 (m, 1 H, H-2); ^{13}C NMR δ 164.80 (COO); 134.9, 132.3, 131.0, 129.2, 128.7, 127.3, 127.2, 125.7 (C arom), 99.6 (C-1), 79.6 (C-2), 78.5 (C-4), 73.7 (C-3), 71.2 (C-5 and C-6), 59.0 (OCH_3), 58.8 (OCH_3). Anal. Calcd for $C_{133}H_{140}O_{42}$: C, 66.25; H, 5.85. Found: C, 65.97; H, 5.82.

$3^A,3^B,3^C,3^D,3^E,3^F,3^G$-Hepta-*O*-methyl-$6^A,6^B,6^C,6^D,6^E,6^F,6^G$-heptachloro-$6^A,6^B,6^C,6^D,6^E,6^F,6^G$-heptadeoxy-β-cyclodextrin (5). A mixture of 165 mg (0.13 mmol) of per-3-*O*-methyl-β-cyclodextrin **1** and 1 mL (excess) of methanesulfonyl chloride in 5 mL of anhydrous DMF was heated at 65 °C for 24 h.[13] Then the solvent was removed at reduced pressure. The residue was dissolved in MeOH and neutralized with 3 M MeONa in MeOH to distroy the *O*-formate esters formed in the reaction, after which it was diluted with water. The precipitate was collected by filtration to yield 175 mg of a brownish powder. The residue was purified by column chromatography (AcOEt–acetone 4–1) to afford 135 mg (74%) of pure **5** as a white powder: mp 260 °C; TLC (CH_2Cl_2–acetone 7–3); R_f 0.33; FAB-MS calcd (M + Na)$^+$ 1385, found 1384; ^1H NMR (CD_3COCD_3) δ 5.03 (s, 1 H, H-1), 4.44 (m, 1 H), 4.17–3.88 (m, 3 H), 3.62 (s, 3 H, OCH_3); ^{13}C NMR (CD_3COCD_3) δ 103.73 (C-1), 83.70, 81.93, 74.38, 73.22 (C-2 to -5), 63.23 (OCH_3), 45.49 (C-6).

$3^A,3^B,3^C,3^D,3^E,3^F,3^G$-Hepta-*O*-methyl-$6^A,6^B,6^C,6^D,6^E,6^F,6^G$-heptaiodo-$6^A,6^B,6^C,6^D,6^E,6^F,6^G$-heptadeoxy-β-cyclodextrin (7). A mixture of 135 mg (0.1 mmol) of chloroderivative **5** and 1.5 g (excess) of NaI in 10 mL of butanone was refluxed for 3 days. After addition of water, the precipitate was collected by filtration to yield 140 mg of iodide **7** used without further purification: mp 253 °C (lit.[37] 235 °C); TLC (CH_2Cl_2–acetone 7–3); R_f 0.4; ^1H NMR δ 4.98 (d, *J* = 3.2, 1 H, H-1), 4.46 (d, *J* = 9.5, 1 H, OH), 3.71 (s, 3 H, OCH_3), 3.75–3.31 (m, 6 H); ^{13}C NMR δ 102.9 (C-1), 83.65, 82.2, 73.5, 71.6 (C-2 to -5), 59.4 (OCH_3), 6.6 (C-6).

$3^A,3^B,3^C,3^D,3^E,3^F,3^G$-Hepta-*O*-methyl-$6^A,6^B,6^C,6^D,6^E,6^F,6^G$-heptadeoxy-β-cyclodextrin (8). To a solution of 95 mg (0.05 mmol) of iodide **7** in 3 mL of DMF was added a large excess of $NaBH_4$ (50 mg). The mixture was heated for 2 h at 70 °C. Then, the solvent was removed under reduced pressure. The residue was triturated with water and extracted with EtOAc. The organic layer was washed with 1 M HCl and then with water. After drying over Na_2SO_4, the solvent was evaporated at reduced pressure to yield 70 mg of a white powder, which was purified by TLC (CH_2Cl_2–acetone 65–35) to afford 45 mg (75%) of pure **8** as a white crystalline powder: mp ~300 °C; TLC (CH_2Cl_2–acetone 7–3); R_f 0.35; FAB-MS calcd (M + Na)$^+$ 1144, obsd 1144; ^1H NMR δ 4.78 (d, *J* = 3.3, 1 H, H-1), 4.42 (d, *J* = 9.4, 1 H, OH), 3.77 (m, 1 H, H-5), 3.71 (s, 3 H, OCH_3), 3.66 (m, 1 H, H-2), 3.47 (m, 1 H, H-3), 3.10 (m, 1 H, H-4), 1.32 (d, *J* = 6.2, 3 H, CH_3); ^{13}C NMR δ 103.1 (C-1), 85.76 (C-4), 83.10 (C-3), 73.91 (C-2), 67.71 (C-5), 59.21 (OCH_3), 17.42 (C-6).

$3^A,3^B,3^C,3^D,3^E,3^F,3^G$-Hepta-*O*-methyl-$6^A,6^B,6^C,6^D,6^E,6^F,6^G$-heptadeoxy-β-cyclodextrin-$2^A,2^B,2^C,2^D,2^E,2^F,2^G$-heptanaphthoate (9). To a solution of 35 mg (0.018 mmol) of **8** in 2.5 mL of dry pyridine was added 75 mg (0.38 mmol–3 equiv) of 2-naphthoyl chloride. The mixture was heated for 1 week at 70 °C. After cooling, water was added, and the mixture was extracted with EtOAc. The organic layer was washed with 1 M HCl and with water. After drying over Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by TLC to yield 25 mg of **9** as an oil which crystallized by addition of MeOH to afford 18 mg (45%) of a white powder: mp ~190 °C; $[\alpha]^{25}_D$ + 407° (*c* 0.29, $CHCl_3$); TLC (CH_2Cl_2–acetone 95–5); R_f 0.44; FAB-MS calcd 2200, found 2200; ^1H NMR δ 8.65 (s, 1 H, H-1′), 8.02 (dd, *J* = 1.2, 8.6, 1 H, H-3′), 7.80–7.76 (m, 3 H, H-4′, H-5′, H-8′), 7.55–7.26 (m, 2 H, H-6′, H-7′), 5.37 (d, *J* = 3.6, H-1), 5.08–5.03 (dd, *J* = 10.1, 1 H, H-2), 4.12 (m, 1 H, H-5), 3.90 (m, 1 H, H-3), 3.47 (m, 1 H, H-4), 3.30 (s, 3 H, OCH_3), 1.54 (d, *J* = 6.1, 3 H, H-6); ^{13}C NMR δ 165.95 (COO), 135.45 (C-2′), 132.4 (C-8′a), 131.3, 129.2, 128.2, 128.0, 127.6, 127.25 (C-4′a), 126.5, 125.15 (10 C arom), 97.75 (C-1), 84.5 (C-4), 80.2 (C-3), 73.9 (C-2), 67.7 (C-5), 60.03 (OCH_3), 16.1 (C-6). Anal. Calcd for $C_{126}H_{126}O_{35}$: C, 68.78; H, 5.77. Found: C, 68.54; H, 5.84.

$6^A,6^B,6^C,6^D,6^E,6^F,6^G$-Heptabromo-$6^A,6^B,6^C,6^D,6^E,6^F,6^G$-heptadeoxy-β-cyclodextrin (10). To a stirred solution heated to 65 °C of 2.27 g (2 mmol) of β-cyclodextrin in 35 mL of DMF was added dropwise 6 mL (170 mmol) of methanesulfonyl bromide.[38] The mixture was stirred 24 h at the same temperature. Then, the solvent was removed and coevaporated with toluene to yield a pale yellow oil which was dissolved in methanol and neutralized with 3 M sodium methoxide in methanol. Addition of crushed ice gave a white precipitate which was filtered off and exhaustively washed with water and methanol to yield 2.5 g (80%) of **10**: mp ~300 °C (li.[15] 205–206 °C); ^1H NMR (DMSO-d_6) δ 6.03 (d, *J* = 6.3, 1 H, OH), 5.89 (s, 1 H, OH), 4.96 (s, 1 H, H-1), 4.00 (m, 1 H), 3.78 (m, 1 H), 3.62 (m, 2 H), 3.35 (m, 2 H); ^{13}C NMR (DMSO-d_6) δ 102.12 (C-1), 84.67, 72.35, 72.10, 71.08 (C-2 to -5), 34.43 (C-6).

β-Cyclodextrin-$6^A,6^B,6^C,6^D,6^E,6^F,6^G$-heptanaphthoate (11). A mixture of 394 mg (0.25 mmol) of bromide **10** and 374 mg (1.92 mmol, 1.1 equiv) of sodium 2-naphthoate in 2.5 mL of HMPA was heated for 3 days at 90 °C. After cooling, the mixture was poured into water, and the precipitated solid was filtered off and washed with water to yield, after drying, 540 mg of a white powder. Fifty milligrams of this product was purified by TLC (CH_2Cl_2–MeOH 8–2) and then crystallized from a mixture of CH_2Cl_2–EtOH 1–1 to afford 20 mg of microcrystals of **11**: mp 250–255 °C; TLC (CH_2Cl_2–MeOH) R_f 0.5; ^1H NMR δ 8.57 (s, 1 H, H-1′), 7.98–7.74 (m, 4 H arom), 7.53–7.49 (m, 2 H arom), 6.27 (s,

1 OH), 5.27 (m, 1 OH), 5.07 (s, 1 H, H-1), 4.94 (m, 1 H), 4.55 (m, 1 H), 4.34 (m, 1 H), 4.07 (m, 1 H), 3.79 (m, 1 H), 3.83 (m, 1 H); ^{13}C NMR δ 165.74 (COO), 135.11, 132.01, 130.82, 129.01, 127.78, 127.28, 126.67, 126.09, 124.68 (10 C arom), 102.46 (C-1), 82.79, 73.43, 73.11, 70.24, 63.29 (C-2 to -6).

2^A,2^B,2^C,2^D,2^E,2^F,2^G,3^A,3^B,3^C,3^D,3^E,3^F,3^G-Tetradeca-*O*-acetyl-6^A,6^B,6^C,6^D,6^E,6^F,6^G-heptabromo-6^A,6^B,6^C,6^D,6^E,6^F,6^G-heptadeoxycyclodextrin (12). A mixture of 500 mg (2 mmol) of bromide **11** and of 5 mL (large excess) of acetic anhydride in 10 mL of pyridine was stirred 24 h at room temperature. After addition of crushed ice, the precipitate was collected and washed with water. After drying, it was recrystallized from MeOH to yield 575 mg (77%) of pure **12**: mp 125 °C (lit.[39] 125–125.5 °C); ^{1}H NMR δ 5.37–5.28 (m, 1 H, H-3), 5.20 (d, J = 3.7, 1 H, H-1), 4.84–4.78 (dd, J = 3.7, 9.8, 1 H, H-2), 4.12 (m, 1 H), 4.83–4.70 (m, 3 H), 2.14–2.04 (s, s, 2 $OCOCH_3$); ^{13}C NMR δ 96.49 (C-1), 78.57, 78.38, 70.23 (C-2 to -5), 33.12 (C-6), 20.59 ($OCOCH_3$).

2^A,2^B,2^C,2^D,2^E,2^F,2^G,3^A,3^B,3^C,3^D,3^E,3^F,3^G-Tetradeca-*O*-acetyl-β-cyclodextrin-6^A,6^B,6^C,6^D,6^E,6^F,6^G-heptanaphthoate (13). (a) From **11**: 50 mg (0.022 mmol) of **11** dissolved in 1 mL of dry pyridine were treated with 0.5 mL of acetic anhydride for 24 h at room temperature. After addition of water and extraction with EtOAc, the organic layer was washed with 1 M HCl and with water and then was dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue (65 mg) was purified by TLC (CH_2Cl_2–acetone 4–1) yielding 20 mg (30%) of pure **13**.

(b) From **12**: A mixture of 216 mg (0.1 mmol) of **12** and 271 mg (1.4 mmol, 2 equiv) of sodium 2-naphthoate in 2 mL of HMPA was heated for 48 h at 90 °C. After cooling, water was added, and the mixture was extracted with EtOAc. The organic layer was washed with water, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by TLC (CH_2Cl_2–acetone 4–1) to afford 160 mg of a powder which was recrystallized from a mixture EtOH–ether to yield 125 mg (45%) of **13** as a white powder: mp 190 °C; $[\alpha]^{25}_D$ +87.5 (c 0.555, $CHCl_3$); TLC (CH_2Cl_2–acetone 7–3) R_f 0.65; FAB-MS (M + H$^+$) calcd 2803, obsd 2804; ^{1}H NMR δ 8.63 (s, 1 H, H-1′), 8.09–8.00 (m, 2 H, H-3′, H-5′ or -8′), 7.88 (d, J = 8.6, 1 H, H-4′), 7.77 (m, 1 H, H-8′ or -5′), 7.49–7.42 (m, 2 H, H-6′, H-7′), 5.47 (m, 1 H, H-3), 5.33 (d, J = 3.6, H-1), 4.97–4.90 (m, 1 H, H-6), 4.88–4.81 (dd, J = 3.6, 9.9, 1 H, H-2), 4.74–4.69 (m, 1 H, H-6), 4.44–4.39 (m, 1 H, H-5), 4.02–3.93 (m, 1 H, H-4), 2.14 (s, 3 H, $OCOCH_3$), 2.07 (s, 3 H, $OCOCH_3$); ^{13}C NMR 170.5 (OCO-CH_3), 169.2 (OCO-CH_3), 165.7 (OCO arom), 135.45 (C-2′), 132.5 (C-8′a), 131.2 (C-8′), 129.4 (C-1′ or -4′), 128.1 (C-5′), 128.0 (C-2′ or -3′), 127.5 (C-4′ or -1′), 126.9 (C-4′a), 126.3 (C-3′ or -2′), 125.2 (C-6′), 96.7 (C-1), 76.9 (C-4), 71.0 (C-3, C-2), 70.1 (C-5), 62.9 (C-6), 20.7 (CH_3). Anal. Calcd for $C_{147}H_{140}O_{56}\cdot 2H_2O$: C, 62.19; H, 5.11. Found: C, 62.16; H, 5.10.

Methyl 6-Bromo-6-deoxy-α-D-glucopyranoside (15). To a stirred solution of 3.9 g (20 mmol) of methyl α-D-glucopyranoside **14** in 75 mL of dry DMF, was added 15.9 g (100 mmol) of methanesulfonyl bromide dropwise.[38] The solution was maintained at 65 °C for 19 h. The DMF was removed under reduced pressure. The residue was dissolved in methanol and neutralized with 3 M sodium methoxide in methanol. The mineral precipitate was filtered off. The solvent was evaporated, and the residue was chromatographed through 50 g of silica gel with a mixture EtOAc–EtOH–H_2O (45–5–3) to yield 4.5 g (87%) of **15** as a well-crystallized product: mp 126 °C. A small sample was recrystallized from ispropyl alcohol: mp 135 °C (lit.[39] 136–137 °C); TLC (EtOAc–EtOH–H_2O 45–5–3) R_f 0.6.

Methyl 2,3,4-Tri-*O*-acetyl-6-bromo-6-deoxy-α-D-glucopyranoside (16). Bromide **15** (500 mg, 1.9 mmol) dissolved in 10 mL of dry pyridine was treated with 5 mL of acetic anhydride for 24 h at room temperature. After addition of crushed ice, the precipitate was collected and recrystallized from MeOH yielding 575 mg (77%) of **16**: mp 127–128 °C (lit.[39] 125–125.5 °C).

Methyl 2,3,4-Tri-*O*-acetyl-α-D-glucopyranoside-6-naphthoate (17). Bromide **16** (191.5 mg, 0.5 mmol) was dissolved in 2.5 mL of HMPA and heated at 90 °C for 24 h. After cooling, water was added, and the mixture was extracted with EtOAc. The organic layer was washed with water, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified through a short column of silica gel with CH_2Cl_2–ether (95–5) as the eluent, to afford 200 mg (84%) of **17** as an amorphous powder: $[\alpha]^{25}_D$ +112° (c 0.385, $CHCl_3$); TLC (CH_2Cl_2–ether 95–5) R_f 0.5; ^{1}H NMR δ 8.61 (s, 1 H, H-1′), 8.07–8.03 (dd, J = 1.6, 8.6, 1 H, H-3′), 7.98–7.95 (m, 1 H, H-5′ or -8′), 7.89–7.85 (d, J = 8.7, 1 H, H-4′), 7.88–7.84 (m, 1 H, H-8′ or -5′), 7.62–7.48 (m, 2 H, H-6′, H-7′), 5.53 (m, 1 H, H-3), 5.20 (m, 1 H, H-4), 4.99–4.91 (m, 1 H, H-2), 4.98 (s, 1 H, H-1), 4.58–4.40 (m, 2 H, H-6), 4.21–4.13 (m, 1 H, H-5), 3.43 (s, 3 H, OCH_3), 2.07, 2.03, 2.01 (3 s, 9 H, 3 $OCOCH_3$); ^{13}C NMR δ 169.8, 169.7, 169.3 (3 $OCOCH_3$), 166.0 (OCO arom), 135.5 (C-2′), 132.3 (C-8′a), 131.1 (C-8′), 129.2 (C-1′ or -4′), 129.1 and 128.05 (C-2′ or -3′ and C-5′), 127.5 (C-4′ or -1′), 126.8 (C-4′a), 126.5 (C-3′ or -2′), 125.0 (C-6′), 96.6 (C-1), 70.7 (C-2), 70.1 (C-3), 68.9 (C-4), 67.2 (C-5), 62.7 (C-6), 55.2 (OCH_3), 20.4 ($OCOCH_3$). Anal. Calcd for $C_{24}H_{26}O_{10}$: C, 60.75; H, 5.52. Found: C, 60.86; H, 5.60.

Spectroscopic Measurements. The UV–vis absorption spectra were recorded on a Kontron Uvikon-940 spectrophotometer. Corrected fluorescence spectra were obtained with a SLM 8000 C spectrofluorometer. Fluorescence quantum yields were determined with PPO in undegassed cyclohexane, ϕ = 0.90 as the standard.[40] All solvents used were of spectroscopic grade. Sample degassing was achieved by the freeze–pump–thaw method (5 cycles).

Steady-state fluorescence anisotropies defined as $r = (I_\parallel - I_\perp)/(I_\parallel + 2I_\perp)$ (where $I_\parallel$ and $I_\perp$ are the fluorescence intensities observed with vertically polarized excitation light and vertically and horizontally polarized emissions, respectively) were determined by the G-factor method.[41]

Time-resolved fluorescence experiments were carried out in both frequency and time domains. In frequency domain we used a multifrequency (0.1–200 MHz) phase-modulation fluorometer described elsewhere[42] with PPO in cyclohexane (τ = 1.27 ns) as a reference. The samples were excited at 325 nm with an Omnichrome He-Cd laser. The number of frequencies used was typically 20. The emission wavelength was selected by means of an interference filter (Balzers) together with a cut-off one (Corion LG-370). In time domain the single-photon timing technique[40] was used with picosecond laser excitation. The laser system (Spectra-Physics) consisted of an Argon-Ion laser (SP 2030), a cavity dumped and synchronously pumped dye laser (SP 375), and a frequency doubler (SP 390), and the excitation wavelength was 300 nm. Detection through a monochromator (Jobin-Yvon H 10) was achieved by means of a microchannel plate photomultiplier (Hamamatsu R 1564-06). A detailed description of the laser system has been reported elsewhere.[43]

Low-temperature measurements (100 K) were performed in specially made 1 cm × 1 cm strain-free quartz cuvettes and with an Oxford DN1704 cryostat with quartz windows. The time needed for the stabilization of the sample temperature was observed to be no less than 45 min, while the preselected temperature (100 K) was attained in the chamber a few minutes after filling the cryostat with liquid nitrogen.

Methods of Calculation and Data Analysis. Critical radii for transfer by the dipolar mechanism were evaluated from Förster's equation, rewritten as[44]

$$R_0 = 0.2108\left[\kappa^2\phi_0 n^{-4}\int_0^\infty I(\lambda)\epsilon(\lambda)\lambda^4 d\lambda\right]^{1/6}$$

with R_0 in Å, where κ^2 is the orientational factor, ϕ_0 is the donor fluorescence quantum yield, n the average refractive index of the medium in the wavelength range where spectral overlap is significant, $I(\lambda)$ the normalized fluorescence spectrum of the donor, $\epsilon(\lambda)$ the acceptor absorption coefficient (in dm^3·mol^{-1}·cm^{-1}), and λ the wavelength in nanometers. A common quantum yield of 0.48 was used for all molecules at 100 K, calculated from the room temperature one (0.40) by the relation $\phi(100\text{ K}) = \phi(290\text{ K})\tau(100\text{ K})/\tau(290\text{ K})$ where the lifetimes are those of the model molecule NAGlu (Tables I and IV). The refractive index used was that of ethanol (1.36).

Fluorescence decay data analysis was carried out by two different methods: nonlinear least squares analysis (LS) and the maximum entropy method (MEM). Details regarding the application of the latter method to the analysis of data obtained from the single-photon timing and phase-modulation techniques were published previously.[24,25]

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(36) Orientational constraints on the energy transfer efficiency, which may exist for the dipole–dipole mechanism, are unimportant here, as shown by the low value of the anisotropy, implying essentially random relative orientation. The assumption of dynamic averaging regime is not valid in a rigid medium, but only an order of magnitude is searched.

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Anomalous Mass Effects in Isotopic Exchange Equilibria

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Abstract: We have carried out a systematic analytical and computational study of the crossover behavior in the isotopic exchange equilibria between dihydrogen and the hydrogen halides. The reactions have been studied for the isotopomers H, D, T, and ^{4}H. The crossover temperatures are related to the H-H and H-X force constants and the masses of the exchanging and nonexchanging hydrogen atoms. When the mass of the hydrogen atom in HX increases, the crossover temperature increases. When the mass of the nonexchanging hydrogen atom in dihydrogen increases, the crossover temperature decreases. Both of these effects are shown to be enthalpy controlled. The change in the crossover temperatures of the reactions $H_2 + 2^*HX$ with m_{*H} is shown to be entropy controlled. Graphical methods are presented which relate the range of force constants in HX molecules to the existence of a crossover in an isotopic exchange with dihydrogen. It is shown that not all isotopomers give the crossover in a given exchange reaction. Exchange reactions which show the crossover for H-D and H-T exchange do not necessarily show the crossover for T-D exchange or mass independent isotope fractionation. Conversely it is shown that some reactions show T-D crossover or mass independent isotope fractionation, without H-D and H-T crossovers. Such reactions have large mass independent isotope fractionation separation factors. The results obtained are illustrative of the type of behavior found in equilibrium and kinetic systems when isotopic substitution in one of the molecular species leads to a large change in the fraction of the total vibrational kinetic energy associated with the exchanging isotopomer.

Introduction

When isotope effects in a chemical system are studied with different isotopes of the same element, the effects are a monotonic function of their relative mass differences. This generalization follows rigorously from the theory of equilibrium[1,2] processes and for rate processes,[3] both within the first quantum approximation. It is in accord with experimental data with a few exceptions. A small number of cases have now been found which do not conform to the above generalization.

Clayton et al.[4] have found $^{17}O/^{16}O$ and $^{18}O/^{16}O$ abundance ratios in carbonaceous meteorites which show a mass independent fractionation compared with other meteoritic and terrestrial materials. Thiemens et al. have found a number of mass independent isotope effects involving the isotopes of oxygen in atom-molecule and radical-radical reactions. The reactions studied by Thiemens proceed through excited states. A recent example is the reaction of photochemically generated oxygen atoms with carbon monoxide to produce carbon dioxide.[5] Valentini et al.[6] have found a mass independent oxygen isotope fractionation in the photolysis of ozone to produce oxygen. While interesting per se and possibly an explanation of Clayton's findings, these anomalous mass effects[7] are not associated with either equilibrium processes nor rate processes within the framework of transition state theory.[8]

Anomalous mass effects have now been found in equilibrium systems. Fujii et al.[9] have found the $^{238}U/^{235}U$ separation factor, 1.3×10^{-3} at 300 K, in the U(IV)-U(VI) exchange reaction is 0.2×10^{-3}, 17%, larger than a linear interpolation between the $^{238}U/^{234}U$ and the $^{238}U/^{236}U$ separation factors in experiments in which all three separation factors were measured concurrently. Dujardin et al.[10] found the $^{238}U/^{235}U$ separation factor, 2.3×10^{-3} at 300 K, in the U(III)-U(IV) exchange reaction to be almost twice the $^{238}U/^{236}U$ separation factor. These anomalous effects are associated with nuclear interactions in ^{235}U in the chemical species U(III) and U(IV) and are discussed elsewhere.[11]

Numerical computations to date of isotope effects in equilibrium and rate processes, within the framework of transition state theory, for systems with arbitrary large quantum effects show no anomalous mass effects other than for systems which show the crossover.[12-14] The crossover temperature is that temperature at which the logarithm of an isotope enrichment factor changes sign.

In a systematic study of isotopic hydrogen exchange reactions as a function of temperature between polyatomic molecules, which do not show the crossover and in which the exchanging hydrogen atom is bonded to an atom with mass greater than ten times that of a proton, Weston[13] found that the ratios, r, of the logarithms of the T/H fractionation factors to the logarithms of the corresponding D/H fractionation factors fell in the narrow range of 1.33-1.44. This was well within the range of an earlier prediction of 1.33-1.55 for the range at 300 K.[15] Weston found small maxima in r in the temperature range 200-500 K. These maxima

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